1 374 780

PATENT SPECIFICATION (11) 1 374 780

(21) Application No. 58664/71 (22) Filed 17 Dec. 1971
(31) Convention Application No. 113 102/70 (32) Filed 18 Dec. 1970 in (19)
(33) Japan (JA)
(44) Complete Specification published 20 Nov. 1974
(51) International Classification G03C 1/06, 5/00//C07C 135/00
(52) Index at acceptance
C2C 20Y 220 227 22Y 30X 30Y 323 32Y 360 362 364 36Y 630 650 699 798 79Y LY
G2C 211 212 242 27Y 304 310 333 362 388 C19Y C20BM C20D C20F C20X

(54) PHOTOGRAPHIC MATERIALS CONTAINING A BIS-AMINIMIDE COMPOUND

(71) We, KONISHIROKU PHOTO INDUSTRY CO. LTD., a Japanese Body Corporate of 1—10, 3-Chome, Nihonbashi-Muro-machi, Chuo-ku, Tokyo, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

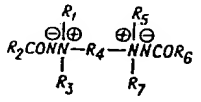
This invention relates to photographic materials containing a bis-aminimide compound as an antistatic agent.

The term " silver halide photographic element " is used herein to define a support carrying at least a layer of a silver halide photographic emulsion. Commercially, the element normally takes the form of a photographic film. Branch-like or fluffy linear spots are frequently formed on the surface of a light-sensitive silver halide photographic element. These spots are so-called static marks, and it is considered that their formation is ascribable to the fact that the surface of the light-sensitive element is statically charged due to friction and this static charge is discharged to excite the light-sensitive element. Troubles derived from such static charge are not limited merely to the formation of static marks but bring about the adhesion of dust onto the surface of the light-sensitive element. Such static troubles are necessarily brought about at substantially all stages where light-sensitive elements undergo friction, e.g. at stages where photographic emulsions are coated on supports, and the resulting film sheets are cut and packed in boxes, or the sheet films are taken out of the boxes and subjected to photographing, and particularly cinefilms are subjected to photographing or handled before development. The static troubles are brought about also at the time when light-sensitive film is released from the rolled-up state. After a film has been prepared by coating a photographic emulsion on a support and drying, it is usually rolled up, and when this rolled film is successively released in order to subject the film to a subsequent step or to printing, static charge is generated between the surface and the back of the film at the moment when the film is released from the roll. Further, when a light-sensitive photographic printing paper is subjected to ferrotype drying, static charge is generated between the surface of the film and the metal surface at the time when the printing paper is taken up, to cause such a phenomenon that the paper cannot be superposed immediately on another one.

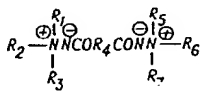
For the prevention of such static troubles, a moisture-absorptive material has frequently been incorporated in a certain layer of the light-sensitive element. This procedure, however, is effective only at the time when the humidity is relatively high and is ineffective under dry ambient conditions when static troubles are brought about frequently. Further, when the humidity is excessively high, the surface of the light-sensitive element containing the moisture-absorptive material becomes sticky.

Many compounds have been proposed as antistatic agents. For application to light-sensitive photographic elements, however, they must not give any detrimental effect to the photographic properties of the light-sensitive element such as sensitivity, gradation, fog and storability. Accordingly, it is extremely difficult to find excellent antistatic agents applicable to light-sensitive silver halide photographic elements.

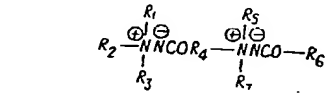
We have now found that bis-aminimide compounds of the general formula (I), (II) or (III) shown below are excellent antistatic agents.



(I)



(II)



(III)

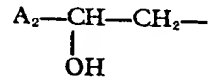
wherein each of R_1, R_3, R_5 and R_7 independently represents an alkyl group having 1 to 4 carbon atoms; each of R_2 and R_6 independently represents (i) an alkyl group which is unsubstituted or substituted by halogen, hydroxy or alkoxy; (ii) an aryl, aralkyl or aryloxyalkyl group, the alkyl portion of which is unsubstituted or hydroxy-substituted, and the aryl portion of which is unsubstituted or ring-substituted; or (iii) a heterocyclic group; and R_4 represents a divalent group

The above-mentioned compounds may be incorporated in a silver halide photographic element at some stage before it is exposed, e.g. in at least one of the following layers: silver halide emulsion layer, sub layer, inter layer, filter layer, antihalation layer, protective layer and backing layer or may be incorporated in a photographic treating bath.

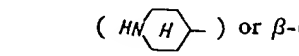
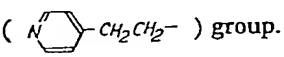
Accordingly the present invention provides (i) a light-sensitive silver halide photographic emulsion containing a bis-aminimide compound as defined above, as an antistatic agent; (ii) a light-sensitive silver halide photographic element which comprises a support carrying a layer of a silver halide emulsion, which element contains as an antistatic agent a bis-aminimide compound as defined above; (iii) a method of giving a silver halide photographic element an antistatic treatment which comprises incorporating in it a bis-aminimide compound as defined above as an antistatic agent; and (iv) a silver halide developing, stop or fixing bath containing a bis-aminimide compound as defined above.

This bis-aminimide compounds defined above impart to a silver halide photographic element a high reduction of static charge effects. The incorporation of the bis-aminimide compound not only does not give any detrimental effect to the sensitivity, gradation and fog of the light-sensitive element but also often displays, depending on the kind of light-sensitive element, such favorable effects as to inhibit fog and enhance the storability of the light-sensitive element. Further, when the compound is applied to a light-sensitive radiographic element, an additional effect is obtained. Namely, the color tone of the developed silver image can be made bluish black, and when the compound is applied to an internal color photographic emulsion, the dispersibility of the coupler used is enhanced to make is possible to obtain a color photographic element having excellent resolution and image graininess.

Referring to the general formulae given above for the bis-aminimide compounds, R_2 or R_6 or both may represent for example (i) an unsubstituted alkyl group, e.g. a methyl group, or a trichloromethyl group or a group of formula



in which A_2 represents an alkoxymethyl or alkyl group, (ii) a phenyl or benzyl group or β-hydroxyphenylethyl group or a group of formula Ph—O—A_1— in which A_1 represents an unsubstituted or hydroxy-substituted alkylene radical and Ph represents a phenyl radical, the benzene ring in said R_2 and R_6 radicals being substituted or unsubstituted, or (iii) a 2-pyrrolyl, 2-furyl, 4-piperidinyl

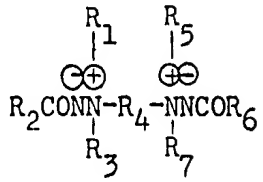
 or β-(4-pyridinyl)ethyl  group.

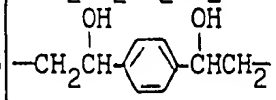
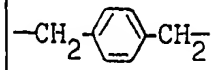
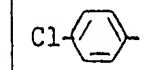
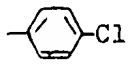
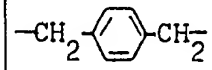
The divalent group R_4 which forms a bridge or part of a bridge between the quaternary nitrogen atoms, preferably consists of a hydrocarbon or oxygen-interrupted hydrocarbon main chain, which may contain one or more pendant hydrocarbon groups or non-hydrocarbon groups or atoms. R_4 may consist of or include a heterocyclic group.

Preferably R_2 and R_6 are the same, R_1 and R_5 are the same and R_3 and R_7 are the same.

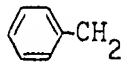
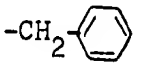
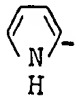
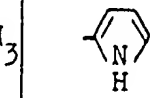
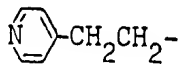
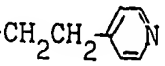
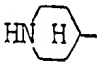
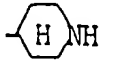
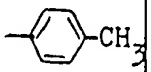
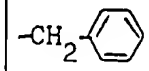
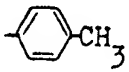
Examples of specific bis-aminimide compounds having the aforesaid general formula are as follows:

General formula (I)



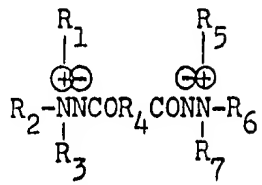
Compound	R_1	R_2	R_3	R_4	R_5	R_6	R_7
1	CH_3	CH_3	CH_3	$-CH_2CH(OH)CH_2OCH_2CH_2OCH_2CH(CH_2Cl)OCH_2CH(OH)CH_2-$	CH_3	CH_3	CH_3
2	CH_3	$C_{15}H_{31}$	CH_3	$-CH_2CH_2CH_2CH_2-$	CH_3	$C_{15}H_{31}$	CH_3
3	CH_3	$C_{11}H_{23}$	C_2H_5		CH_3	$C_{11}H_{23}$	C_2H_5
4	CH_3	$C_{15}H_{31}$	CH_3	$-CH_2CH(OH)CH_2OCH_2CH_2-$	CH_3	$C_{15}H_{31}$	CH_3
5	CH_3	$C_{15}H_{31}$	CH_3		CH_3	$C_{15}H_{31}$	CH_3
6	CH_3		CH_3	$-CH_2CH_2CH_2CH_2-$	CH_3		CH_3
7	CH_3		CH_3		CH_3		CH_3

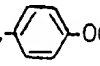
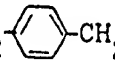
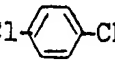
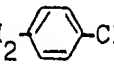
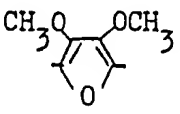
(Continued.....)

8	CH_3	CCl_3	CH_3	$-CH_2CHCH_2OCH_2CH_2OCH_2CHCH_2-$ (OH, OH)	CH_3	CCl_3	CH_3
9	CH_3		CH_3	$-CH_2CHCH_2OCH_2CH_2OCH_2CHCH_2-$ (OH, OH)	CH_3		CH_3
10	CH_3		CH_3	$-CH_2CHCH_2O-C_6H_4-OCH_2CHCH_2-$ (OH, OH)	CH_3		CH_3
11	CH_3		CH_3	$-CH_2CHCH_2OCH_2CHOCH_2CHCH_2-$ (OH, CH_3, OH)	CH_3		CH_3
12	CH_3		CH_3	$-CH_2CHCH_2OCH_2CH_2CH_2CH_2OCH_2CHCH_2-$ (OH, OH)	CH_3		CH_3
13	CH_3		CH_3	$-CH_2CHCH_2OCH_2-C_6H_4-CH_2OCH_2CHCH_2-$ (OH, OH)	CH_3		CH_3
14	CH_3	$C_{11}H_{23}$	CH_3	$-CH_2-C_6H_4-OCH_2CHCH_2-$ (OH)	CH_3		CH_3
15	CH_3		CH_3	$-CH_2CHCH_2OCH_2CH_2-$ (OH)	CH_3		C_2H_5
16	CH_3	$C_{11}H_{23}$	CH_3	$-CH_2CHCH_2OCH_2CH_2OCH_2CHCH_2-$ (OH, OH)	CH_3		CH_3

Compound	Elementary analysis (%)							
	Calculated				Found			
	C	H	N	Halogen	C	H	N	Halogen
1	48.45	8.35	11.90	7.53	48.72	8.25	11.50	7.33
2	73.78	12.70	8.61		74.00	12.56	8.62	
3	71.67	11.05	8.30		71.47	11.20	8.40	
4	70.64	12.15	8.04		70.76	12.26	8.15	
5	78.45	11.82	8.01		78.10	12.15	8.26	
6	58.54	6.25	12.41	15.41	58.48	6.16	12.32	15.21
7	72.22	7.02	13.01		72.10	7.06	13.09	
8	32.84	4.82	9.58		32.76	4.69	9.72	
9	63.37	7.98	10.56		63.31	8.01	10.42	
10	59.07	6.87	15.90		59.21	6.99	15.50	
11	55.62	7.31	11.28		55.61	7.21	11.50	
12	61.20	8.22	14.28		61.72	8.19	14.50	
13	60.99	8.53	14.23		60.71	8.92	14.01	
14	70.07	9.34	9.61		70.51	9.40	9.29	
15	62.00	7.92	15.72		61.98	8.02	15.70	
16	64.10	9.72	9.65		64.30	9.60	9.55	

General formula (II)



Compound	R_1	R_2	R_3	R_4	R_5	R_6	R_7
17	CH_3	$C_8H_{17}OCH_2CH(OH)CH_2-$	C_2H_5		CH_3	$-CH_2CH(OH)CH_2OC_8H_{17}$	C_2H_5
18	CH_3	C_8H_{17}-  -$OCH_2CH(OH)CH_2-$	CH_3	$-(CH_2)_4-$	CH_3	$-CH_2CH(OH)CH_2O$-  -C_8H_{17}	CH_3
19	CH_3	$C_8H_{17}OCH_2CH(OH)CH_2-$	CH_3	$-CH_2$-  -CH_2-	CH_3	$-CH_2CH(OH)CH_2OC_8H_{17}$	CH_3
20	CH_3	CH_3	CH_3	$-(CH_2)_8-$	CH_3	CH_3	CH_3
21	CH_3	Cl-  -CH_2-	CH_3	$-(CH_2)_4-$	CH_3	$-CH_2$-  -Cl	CH_3
22	CH_3	C_5H_{11}	CH_3		CH_3	C_5H_{11}	CH_3
23	CH_3	$C_6H_{13}CH(OH)CH_2-$	CH_3		CH_3	$-CH_2CHC_6H_{13}$ (OH)	CH_3

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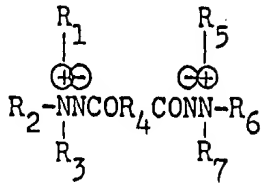
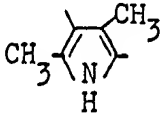
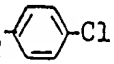
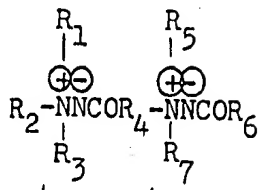
General formula (II)

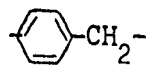
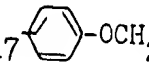
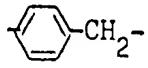
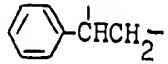


Compound	R_1	R_2	R_3	R_4	R_5	R_6	R_7
24	CH_3	$C_{12}H_{25}OCH_2CH(OH)CH_2$	CH_3		CH_3	$CH_2CH(OH)CH_2OC_{12}H_{25}$	CH_3
25	CH_3	$C_8H_{17}OCH_2CH(OH)CH_2$	CH_3		CH_3	$CH_2CH(OH)CH_3$	CH_3
26	CH_3	$C_8H_{17}OCH_2CH(OH)CH_2$	CH_3		CH_3	CH_3	CH_3
27	CH_3	CH_3	CH_3	$-(CH_2)_4-$	CH_3	CH_2-  -Cl	CH_3
28	CH_3	$C_6H_{13}CH(OH)CH_2$	CH_3		CH_3	$CH_2CH(OH)C_{10}H_{21}$	CH_3

Compound	Elementary analysis (%)							
	Calculated				Found			
	C	H	N	Halogen	C	H	N	Halogen
17	66.42	10.22	8.61		66.60	10.01	8.21	
18	70.91	9.57	7.19		70.56	9.40	7.31	
19	66.42	10.22	8.61		66.21	10.50	8.71	
20	61.11	10.90	17.82		61.21	10.99	17.51	
21	60.12	6.73	11.69		60.90	6.60	11.50	
22	67.65	9.81	14.35		67.21	9.75	14.50	
23	60.40	9.42	10.06		60.56	9.31	10.26	
24	67.07	10.86	9.31		67.21	10.75	9.21	
25	66.39	8.54	10.32		66.21	8.45	10.50	
26	65.79	8.92	11.80		65.31	9.05	11.60	
27	41.40	7.92	15.19	9.61	41.01	8.15	15.01	9.82
28	68.29	10.39	9.96		68.50	10.29	10.01	

General formula (III)



Compound	R_1	R_2	R_3	R_4	R_5	R_6	R_7
29	CH_3	$C_6H_{13}CH(OH)CH_2-$	CH_3		CH_3	$C_{11}H_{23}$	CH_3
30	CH_3	C_8H_{17}  $-OCH_2CH(OH)CH_2-$	C_2H_5		CH_3	$C_{15}H_{31}$	CH_3
31	CH_3		CH_3	$-CH_2CH_2-$	CH_3		CH_3
32	CH_3	$C_{12}H_{25}OCH_2CH(OH)CH_2-$	CH_3	$-CH_2CH_2-$	CH_3		CH_3
33	CH_3	$CH_3CH(OH)CH_2-$	CH_3	$-CH_2CH_2-$	CH_3	$-CH_2$ 	CH_3

	Elementary analysis (%)					
	Calculated			Found		
Compound	C	H	N	C	H	N
29	70.28	10.69	10.25	70.50	10.80	10.15
30	73.55	10.47	7.46	73.40	10.48	7.66
31	66.31	7.59	14.06	66.10	7.75	14.21
32	63.50	9.87	10.97	63.60	10.05	11.21
33	61.69	8.63	15.99	61.31	9.05	16.01

The bis-aminimide compounds of the aforesaid general formulas can be synthesized according to the methods disclosed in R. W. H. Berry & P. Brocklehurst: "J. Chem. Soc." 2264 (1964); R. L. Hinman & M. C. Flores: "J. Org. Chem.", *24* 660 (1959); and R. C. Slagel: "J. Org. Chem.", *33* 1374 (1968).

Typical procedures for synthesizing the abovementioned compounds are set forth in the following Synthesis Examples.

Synthesis Example 1.

Synthesis of the exemplified compound (2):

$$2(CH_3)_2NNHCOC_{15}H_{31} + I(CH_2)_4I \longrightarrow (C_{15}H_{31}CONH\overset{\oplus}{\underset{CH_3}{\underset{|}{N}}}CH_2CH_2)_2\ 2I^{\ominus}$$

(1)

$$(C_{15}H_{31}CONH\overset{\oplus}{\underset{CH_3}{\underset{|}{N}}}CH_2CH_2)_2\ 2I^{\ominus} + 2NaOH \longrightarrow (C_{15}H_{31}CO\overset{\ominus}{N}\overset{\oplus}{\underset{CH_3}{\underset{|}{N}}}CH_2CH_2)_2 + 2NaI + 2H_2O$$

(2)

7.75 Grams of 1,4-diiodobutane and 17.9 g of N,N-dimethyl-N'-hexadecanoylhydrazine were dissolved in 20 ml of dioxane, and the resulting solution was reacted at 73°C. for 48 hours. After completion of the reaction, the liquid reaction mixture was concentrated, and the concentrate was dissolved in 20 ml of methanol. To the resulting solution was added 300 ml. of ether to deposit white crystals, which were then recovered by filtration and repeatedly recrystallized from a methanol-ether mixture to obtain crystals of bisacylhydrazinium iodide (1), m.p. 109—110°C., yield 90.2%.

Elementary analysis:

Found (%)	C: 52.86	H: 9.25	N: 6.36	I: 28.05
Calculated (%)	C: 52.97	H: 9.34	N: 6.18	I: 27.98

(for $C_{40}H_{84}N_4O_2I_2$)

10 Grams of the thus obtained bisacylhydrazinium iodide was added to a solution of 0.5 g. of sodium hydroxide in a mixed solvent comprising 50 ml. of water and 20 ml. of methanol. After allowing to stand for about 30 minutes, the resulting mixture was concentrated, freed from the methanol and then extracted 3 times with 80 ml. of chloroform. The chloroform layer was washed 3 times with 30 ml. of a saturated aqueous sodium chloride solution, dehydrated with anhydrous sodium sulfate and then concentrated to form crystals. Subsequently, the crystals were recrystallized from petroleum benzine to obtain the bis-aminimide compound (2), yield 97.8%, m.p. 43—44°C.

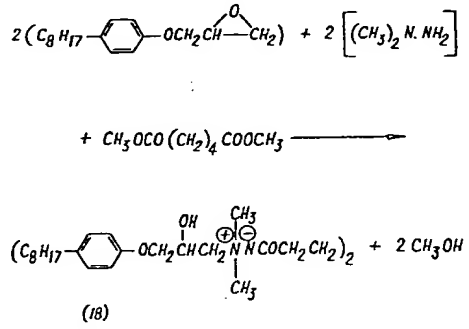
Elementary analysis:

Found (%)	C: 74.00	H: 12.56	N: 8.62
Calculated (%)	C: 73.78	H: 12.70	N: 8.61

(for $C_{40}H_{82}N_4O_2$)

Synthesis Example 2.

Synthesis of the exemplified compound (18):



(18)

31.5 Grams of p-octylphenyl glycidyl ether, 7.20 g. of N,N-dimethylhydrazine and 8.81 g. of dimethyl adipate were dissolved in 40 ml. of isopropyl alcohol, and the resulting solution was reacted at room temperature for 6 days. After completion of the reaction, the liquid reaction mixture was concentrated, and the concentrate was dissolved in 1 liter of water. The resulting solution was washed 4 times with 100 ml. of ether, and the water layer was concentrated to obtain the bis-aminimide compound (18) in the form of an oil, yield 89.5%.

Elementary analysis:

Found (%)	C: 70.56	H: 9.40	N: 7.31	
Calculated (%)	C: 70.91	H: 9.57	N: 7.19	

(for $C_{44}H_{74}N_4O_6$)

For incorporation of any of the bis-aminimide compounds having the aforesaid general formulae into the silver halide emulsion layer, sub layer, inter layer, filter layer, antihalation layer, protective layer or backing layer of a light-sensitive silver halide photographic element, the compound may be dissolved in a suitable solvent such as water or an alcohol and the solution incorporated in said layer or applied by spraying onto the surface of the light-sensitive element, or the light-sensitive element is immersed in said solution. Further, the bis-aminimide compounds may be in-

corporated into a developing solution, stop solution, fixing solution, water mark-preventing solution or the like treating bath. (A water mark-preventing solution contains an agent to decrease surface tension. It serves to prevent formation of water marks on the films). The preferred proportion of bis-aminimide compound is 0.1 mg. to 1 g. per square metre of the light-sensitive element, though the amount varies depending on the kinds of the compound and of the layer in which the compound is to be incorporated.

The following Examples illustrate the invention.

Example 1.

Each of the exemplified compounds (2), (5), (10), (17), (19), (23) and (30) was dissolved in ethyl alcohol to form a 1% solution. This solution was spray-coated on the surface of a high speed roentgen film and then dried to prepare a sample. On the other hand, the said high speed roentgen film was dipped in the above-mentioned solution for 1 minute and then dried to prepare another sample. For comparison, two control samples were prepared in the same manner as above, except that the above-mentioned treatment was not effected or was effected by use of ethanol only. The thus prepared samples including an untreated roentgen film were allowed to stand for 24 hours under conditions of RH 30% and 25°C., rubbed on the surfaces with nylon and polyester cloths, and then developed, without exposure, according to an ordinary procedure by use of a radiographic developing solution. Subsequently, the developed samples were individually scanned with a Sakura Densitometer (a product of Konishiroku Photo Industry Co., Ltd.) to measure the average blackening values. The amount of developed silver (by X-ray analysis) and specific surface resistivity of the samples were measured. The results obtained were as set forth in Table 1.

Table 1

Sample No.	Antistatic agent	Spray coating			Dip coating		
		Average density measured by densitometer	Amount of developed silver ($mg/100cm^2$)	Specific surface resistivity (Ω)	Average density measured by densitometer	Amount of developed silver ($mg/100\ cm^2$)	Specific surface resistivity (Ω)
1	Non-treatment	1.82	65.2	10^{14}	1.72	59,1	10^{14}
2	Ethanol containing no antistatic agent	1.73	59.9	10^{14}	1.65	48.9	10^{14}
3	Exemplified compound 2	0.08	2.6	10^{12}	0.04	1.3	10^{12}
4	Exemplified compound 5	0.07	2.1	10^{12}	0.05	1.8	10^{12}
5	Exemplified compound 10	0.05	1.6	10^{11}	0.03	1.2	10^{11}
6	Exemplified compound 17	0.04	1.2	10^{11}	0.03	1.1	10^{11}
7	Exemplified compound 19	0.07	2.4	10^{12}	0.05	2.0	10^{12}
8	Exemplified compound 23	0.05	1.8	10^{12}	0.03	1.4	10^{12}
9	Exemplified compound 30	0.04	1.4	10^{11}	0.03	1.0	10^{11}

As is clear from Table 1, the sample treated with the solvent containing no exemplified compound and the untreated sample had high average density values gave a large amount of developed silver, and showed a considerable increase in fog density due to formation of static marks, whereas no formation of static marks was observed in the samples according to the present invention (Samples 3 to 9).

On the other hand, these samples were exposed to light, developed at 20°C. for 4 minutes and 30 seconds with a strongly alkaline roentgen film developer containing 1-phenyl-3-pyrazolidone hydroquinone (PQ), and then measured for speed and fog. Further, the samples were subjected to sensitometry after incubation for 3 days in a thermostat chamber kept at 55°C. and under conditions of 50°C. and RH 80%. The results obtained were as set forth in Table 2.

Table 2

Sample No.	Spray coating			Dip coating						
	Relative speed	Relative gamma	Fog	Relative speed	Relative gamma	Fog	After incubation at 55°C. for 3 days		After incubation at 50°C. and RH 80% for 3 days	
							Relative speed	Fog	Relative speed	Fog
1	100	1.0	0.13	100	1.0	0.15	100	0.24	100	0.19
2	101	1.1	0.13	109	1.1	0.14	102	0.30	88	0.18
3	103	1.0	0.13	111	1.0	0.13	108	0.23	100	0.18
4	108	1.1	0.12	105	1.0	0.14	103	0.26	101	0.19
5	100	1.1	0.12	105	1.1	0.14	102	0.23	99	0.16
6	100	1.0	0.13	102	0.99	0.13	100	0.22	98	0.16
7	103	1.0	0.13	101	1.0	0.14	100	0.25	103	0.15
8	100	1.0	0.11	100	0.98	0.12	99	0.26	99	0.17
9	100	1.0	0.12	103	1.0	0.14	100	0.23	100	0.16

From Table 2, it is understood that even when incubated not only at normal temperature but also at high temperature and humidity, the samples according to the present invention (Samples 3 to 9) did not suffer loss of speed, gradation and resistance to fog. In addition, the color tone of the developed silver changed to bluish black to give favorable results.

Example 2.

Each of the exemplified compounds 3, 6, 9, 15, 20, 25, 29 and 33 was dissolved in a 4% solution of sodium decyl-isoamyl succinate-2-sulfonate so that the concentration of the compound became 2%, and 20 cc. of the resulting solution was added to 1 liter of a 2% gelatin solution to be used as a protective layer. Subsequently, the solution was coated as a protective layer on a high sensitivity roentgen film. Samples prepared in the above manner and a sample having a protective layer containing no exemplified compound were subjected to the same tests as in Example 1 to obtain the results as set forth in Table 3.

Table 3

Sample No.	Antistatic agent	Antistatic property: Average density measured by densitometer	Antistatic property: Amount of developed silver (mg/100 cm^2)	Photographic properties: Immediately after preparation: Relative speed	Immediately after preparation: Relative gamma	Immediately after preparation: Fog	After incubation at 55°C. for 3 days: Relative speed	After incubation at 55°C. for 3 days: Fog	After incubation at 50°C. and RH 80% for 3 days: Relative speed	After incubation at 50°C. and RH 80% for 3 days: Fog
10	Protective layer containing no antistatic agent	1.58	39.2	100	1.00	0.12	100	0.23	100	0.15
11	Exemplified compound 3	0.13	4.0	104	1.05	0.11	101	0.24	100	0.17
12	Exemplified compound 6	0.11	3.3	101	1.02	0.10	100	0.20	100	0.16
13	Exemplified compound 9	0.12	3.9	102	1.00	0.10	105	0.23	103	0.16
14	Exemplified compound 15	0.14	4.2	100	1.00	0.11	102	0.22	100	0.15
15	Exemplified compound 20	0.11	3.2	99	1.01	0.09	108	0.18	110	0.12
16	Exemplified compound 25	0.11	3.3	98	1.02	0.10	107	0.17	115	0.12
17	Exemplified compound 29	0.13	4.1	101	1.00	0.12	100	0.21	100	0.16
18	Exemplified compound 33	0.12	4.0	105	1.00	0.11	101	0.20	105	0.15

As is clear from Table 3, it is understood that in the samples according to the present invention (Samples 11 to 18) formation of static marks was prevented without adverse effect on the photographic properties of the film.

Example 3.

To 1 liter of a green-sensitive high sensitivity color photographic silver iodobromide emulsion was added 10 cc. of a 5% methanol solution of each of the exemplified compounds 2, 4, 8, 15, 18 and 31. To the emulsion was further added a solution of 20 g of an internal color photographic magenta coupler 1-(4'-phenoxy-3'-sulfophenyl)-3-heptadecyl-5-pyrazolone in a 1N-caustic soda solution which had been adjusted to pH 6.8 by addition of citric acid. Subsequently, the emulsion was coated on a cellulose triacetate film base and then dried. Samples prepared in the above manner and a sample not containing any exemplified compound, were subjected to the same tests as in Example 1, except that in this example, the average density value was measured by using a green filter as a light source of the densitometer, and the development was effected by an ordinary procedure using diethyl p-phenylenediamine as the developing agent. The results obtained were as set forth in Table 4.

Table 4

Sample No.	Antistatic agent	Antistatic property: Average density measured by densitometer	Antistatic property: Specific surface resistivity (Ω)	Photographic properties: Immediately after preparation: Relative speed	Relative gamma	Fog	After incubation at 50°C. for 3 days: Relative speed	Fog
19	None	0.67	10^{12}	100	1.00	0.12	100	0.22
20	Exemplified compound 2	0.20	10^{11}	101	1.01	0.13	100	0.22
21	Exemplified compound 4	0.23	10^{10}	100	1.00	0.15	100	0.20
22	Exemplified compound 8	0.21	10^{10}	103	1.00	0.13	105	0.21
23	Exemplified compound 15	0.22	10^{11}	100	1.01	0.15	100	0.23
24	Exemplified compound 18	0.20	10^{11}	99	1.08	0.12	100	0.20
25	Exemplified compound 31	0.21	10^{11}	100	1.00	0.12	99	0.21

From Table 4, it is understood that by addition of the exemplified compounds to the emulsion formation of static marks was prevented in the samples according to the present invention. Also the dispersibility of the formed dyes was improved and there was no detrimental effect on photographic properties.

Example 4.

To a 5% aqueous gelatin solution containing an antihalation dye was added 2 cc. of a 2% aqueous solution of each of the exemplified compounds 2, 3, 10 and 18. The resulting solution was charged with 3cc. of a 5% saponin solution and then coated on a cellulose triacetate film base, followed by drying. On the opposite side of the film base was coated a high speed photographic emulsion for negative and a protective layer was formed on the resulting emulsion layer by application of a gelatin solution incorporated with 300 mg. per liter of said solution of the above-mentioned exemplified compound. Samples prepared in the above manner were subjected to the same tests as in Example 1 to obtain the results set forth in Table 5.

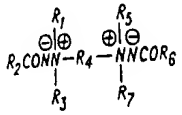
Table 5

Sample No.	Antistatic agent	Antistatic property		Photographic properties				
				Immediately after preparation			After incubation at 50°C. for 3 days	
		Average density measured by densitometer	Amount of developed silver (mg/100 cm^2)	Relative speed	Relative gamma	Fog	Relative speed	Fog
26	None	1.10	33.6	100	1.00	0.12	100	0.30
27	Exemplified compound 2	0.12	3.8	100	1.00	0.11	102	0.28
28	Exemplified compound 3	0.10	3.2	100	1.02	0.12	105	0.30
29	Exemplified compound 10	0.08	2.8	98	1.00	0.14	100	0.28
30	Exemplified compound 18	0.12	3.3	97	1.01	0.11	101	0.28

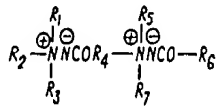
As is clear from Table 5, formation of static marks was prevented in the samples according to the present invention (Samples 27 to 30) and the photographic properties of the samples were not adversely affected.

WHAT WE CLAIM IS:—

1. A light-sensitive silver halide photographic emulsion containing as an antistatic agent a bis-aminimide compound of the general formula



(I)



(III)

wherein each of R_1, R_3, R_5 and R_7 independently represents an alkyl group having 1 to 4 carbon atoms; each of R_2 and R_6 independently represents (i) an alkyl group which is unsubstituted or substituted by halogen, hydroxy or alkoxy, (ii) an aryl, aralkyl or aryloxyalkyl group the alkyl portion of which is unsubstituted or hydroxy-substituted, and the arvl portion of which is unsubstituted or ring-substituted; or (iii) a heterocyclic group; and R_4 represents a divalent group.

2. An emulsion according to claim 1 wherein R_2 or R_6 or both represents a phenyl or benzyl group or β-hydroxyphenylethyl group or a group of formula Ph—O—A_1— in which A_1 represents an unsubstituted or hydroxy-substituted alkylene radical and Ph represents a phenyl radical, the benzene ring in said R_2 and R_6 radicals being substituted or unsubstituted, or a 2-pyrrolyl, 2-furyl, 4-piperidinyl or β-(4-pyridinyl)ethyl group, a trichloromethyl group or a group of formula

$$A_2—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_2$$

in which A_2 represents an alkoxymethyl or alkyl group.

3. An emulsion according to claim 1 or 2 wherein R_2 and R_6 are the same.

4. An emulsion according to any preceding claim wherein R_1 and R_5 are the same.

5. An emulsion according to any preceding claim wherein R_3 and R_7 are the same.

6. An emulsion according to any preceding claim wherein R_4 represents a divalent radical consisting of a hydrocarbon or oxygen-interrupted hydrocarbon main chain, which may contain one or more pendant hydrocarbon groups or non-hydrocarbon groups or atoms.

7. An emulsion according to any preceding claim wherein R_4 consists of or includes a divalent heterocyclic group.

8. An emulsion according to claim 1 wherein the bis-aminimide compound is any one of the compounds (1) to (33) specifically hereinbefore named.

9. An emulsion according to claim 1 substantially as described in Example 3.

10. A light-sensitive silver halide photographic element which comprises a support carrying a layer of a silver halide emulsion, which element contains as an antistatic agent a bis-aminimide compound defined in any one of claims 1—8.

11. An element according to claim 10 in which the antistatic agent is present in the emulsion layer.

12. An element according to claim 10 or 11 which further contains a sub layer, inter layer, filter layer, antihalation layer, protective layer or backing layer.

13. An element according to claim 12 wherein said layer contains as an antistatic agent a compound defined in any one of claims 1—8.

14. A light-sensitive photographic material containing a compound defined in claim 1, substantially as described in any one of the Examples.

15. A method of giving a silver halide photographic element an antistatic treatment, which comprises incorporating in it a compound defined in any one of claims 1—8 as an antistatic agent.

16. A method according to claim 15 wherein the antistatic agent is incorporated in the element before it is exposed.

17. A method according to claim 15 wherein the exposed silver halide photographic material is treated with a developing, stop or fixing bath containing the antistatic agent.

18. A method according to claim 15 or 16 wherein a solution of the antistatic agent is sprayed onto the photographic element.

19. A photographic element treated by a method claimed in any one of claims 15—18.

20. A silver halide developing, stop or fixing bath containing a compound defined in any one of claims 1—8.

J. A. KEMP & CO.,
Chartered Patent Agents,
14, South Square,
Gray's Inn,
London, WC1R 5EU.

Reference has been directed in pursuance of Section 9, subsection (1) of the Patents Act 1949, to patents Nos. 1,265,163 and 1,178,697.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1974.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.